APPLICATION OF LIGHT EMITTING DIODES AND PHOTOTRANSISTORS TO PHOTOMETERS

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APPLICATION OF LIGHT EMITTING DIODES AND

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SUMMARY

In photometry, the production of monochromatic light requires the use of bulky and complex monochromating systems. Whether the monochromater is a prism, a filter or a grating, a significant portion of the radiant energy is absorbed before it reaches the sample cell. A rather involved and expensive power supply is necessary to produce sufficient radiant energy with acceptable stability. This requirement nearly eliminates the possibility of constructing a portable photometer for the conduct of en-site analyses. These problems can be neatly circumvented through the use of two recent developments from the field of electronics: the light emitting diode (LED) and the phototransistor (PT). The LED is a gallium arsenide diode which emits relatively monochromatic light when biased in the forward direction, using two flashlight cells as a power supply. The PT, a device through which current flows in proportion to the intensity of the incident light, can be coupled to an integrated circuit amplifier to drive a millivoltmeter. This phenomenally simple, battery powered device can replace a bulky, expensive photomultiplier tube and associated circuitry for additional weight and cost savings.

The ruggedness, stability, low cost and low power requirements of the LED and the PT render them ideally suited for the construction of a simple, inexpensive and completely portable photometer. Their small size and weight permit them to be affixed directly to the sample cell, forming rugged, stable modules. These modules can be constructed

with sample cell lengths as long as 40 cm, allowing the use of long path photometry. By enclosing the cell module in a lightproof box, and adding a control module, containing all necessary power supplies, controls, an amplifier and a meter, the portable photometer is complete.

The operation of the solid state photometer is quite straight forward. Absorbances are read against a reference solution and the data are treated using a calibration curve technique. The device was tested with regard to stability, linearity of response, reproducibility of readings, light tightness and portability. The photometer was found to be quite adequate in all areas.

The most severe limitation at present is that a limited number of LEDs are available which emit in the visible spectrum. However, considerable research is being conducted in this area, and it is only a matter of time until adequate coverage is obtained.

CHAPTER I

INTRODUCTION

General

The widespread interest in environmental pollution today makes it highly desirable for one to have the capability to conduct on-site analysis of samples. Unfortunately, the bulk, complexity and power requirements of the majority of analytical instruments make on-site analysis impractical. The purpose of this work has been to investigate the feasibility of applying solid state electronic devices to photometers in order to reduce those limiting factors to practical levels. The use of light emitting diodes in photometers was suggested by R. L. Barnes as a research proposal (1). The decision to apply phototransistors was arrived at during this research.

Typical Photometers

In order to streamline and simplify photometers, it is necessary to have a working understanding of the construction and operation of the instruments presently in common use. The analytical method of photometry is based upon the absorption of light by the sample under consideration. In a typical photometer (Figure 1), radiant energy from a light source is passed through a monochromating device and then through the sample solution, where a portion of the light is absorbed. The remaining light emerges from the sample cell

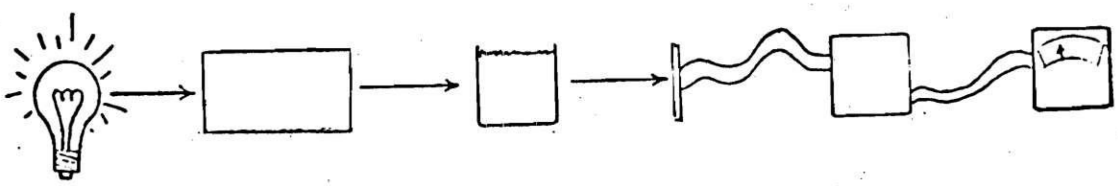


Figure 1. A Typical Photometer.

and strikes a photodetector. The signal from the photodetector is then amplified and displayed on a metering device. Three elements of the typical photometer, grossly simplified in the above description, may share the major responsibility for the bulkiness, complexity and high power requirements. These are the light source, the monochromater and the detection system. A discussion of each of these elements and their shortcomings follows.

Light Source

The most commonly used light source is the incandescent lamp. This source emits compound, i. e., heterochromatic light, as well as considerable amounts of heat. Because of large losses of radiant energy, which will be discussed later, the source must emit light at relatively high levels of intensity. If the light source is to be operated from a portable power source, one encounters difficulties. The power drain is considerable and stability of the level of intensity is not reliable unless several large lead storage batteries are used. This almost completely negates portability. Adequate stability can be achieved through regulated power supplies, but these are complex and usually depend on 115 VAC power.

Monochromaters

In order to assure adherence to the Lambert-Beer Law, it is necessary that the light passing through the sample be relatively monochromatic. This is usually achieved by passing the light through a filter, a grating or a prism. In the process, considerable amounts of light are either absorbed, diffracted or dispersed. Additional quantities of light are absorbed by the collimating optics. Filters are the simplest means of achieving monochromacy. The selection of a filter is usually a compromise between monochromacy and transmittance. The higher the degree of monochromacy, the larger the amount of light absorbed by the filter. One of the major disadvantages of filters is that a different filter must be used for each wavelength desired. Gratings can be used to achieve monochromacy, but scattering and interference from other spectral orders may contaminate the emerging light. Prisms may be used to disperse the light into a spectrum from which the desired wavelength is selected. The degree of monochromacy depends on the thickness of the base of the prism and the width of the slit. Significant amounts of radiant energy may be absorbed by the prism. Regardless of the type of monochromating system used, losses of radiant energy require that the light source emit sufficiently high intensity light so that the emerging light may pass through the sample and be detected. Reduction or elimination of light losses in a monochromating system would be one means to lower the requirements on the light intensity.

Detection System

It is possible to use any device that is sensitive to light as a photodetector. Indeed, an instrument can be constructed using a photovoltaic cell as a detector. Since the photovoltaic cell produces its own emf, it can drive a galvanometer directly. The major drawbacks to this device are that large amounts of light must strike the cell and that memory effects render the response of the cell unreliable. Phototubes provide a much more viable detection capability. Light striking the photocathode causes the ejection of electrons, which are attracted to the anode. The resulting current is proportional to light intensity. A major improvement to the phototube is the photomultiplier tube, the device most commonly used in commercial instruments. It is highly sensitive to low light levels, possesses fast response and contains internal amplification of the detected signal with excellent linearity. The major shortcoming of the photomultiplier tube is the need for a high voltage power supply (600-3000 volts)(2). This restricts practical portability.

<u>Interaction of Elements</u>

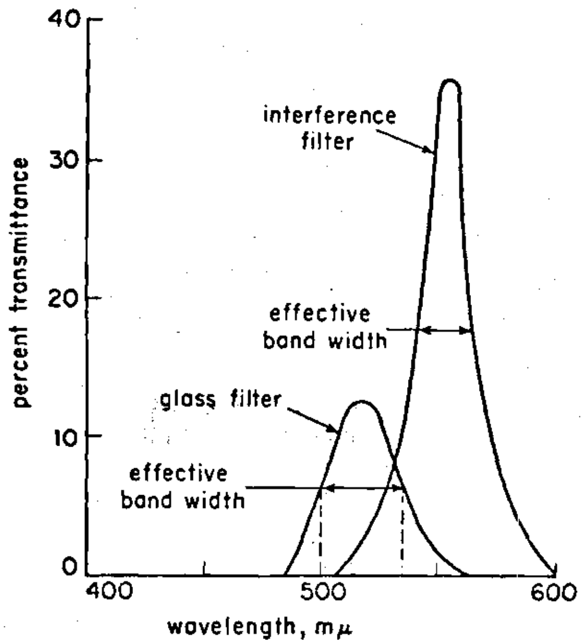
The design of a photometer, or any other device, is essentially a trade-off or compromise between the advantages and the disadvantages of the components involved. Depending on the desired application and physical parameters involved, one can make simplifications in the device. If sensitivity of the determination is the objective, one may increase the path length of the cell. If this is done, the sensitivity of the detecting system must be increased or the amount of light transmitted to the cell must be increased. The sensitivity of the detecting system may be increased through amplification, but only to the point where the signal to noise ratio becomes significant. Light intensity may be increased by raising the intensity of emitted light or by reducing the amount of light lost in the monochromater. Power source limitations or physical limitations of the light source may restrict the intensity of the emitted light. If the monochromator employs filters, a filter with a wider band-pass may be used, increasing the transmitted light, but decreasing the monochromacy. A better trade-off might be achieved by employing a grating or a prism, but use of these devices increases the complexity of the instrument. The designer, then, must consider the pros and cons of all of the components available and decide what level of compromise is acceptable, commensurate with his desired objectives. In order to circumvent a portion of this problem, it is well to examine devices not commonly used in photometric applications and discover what benefits may be derived from their use. To this end, the field of solid state electronics appears to be fertile ground.

Solid State Electronic Technology

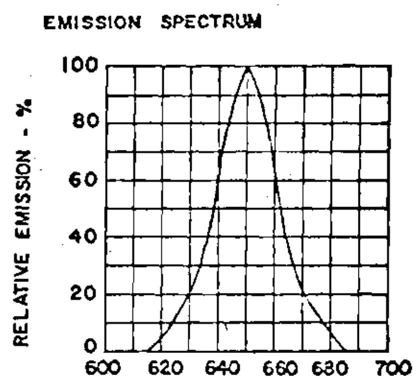
The rapid growth of solid state technology since the 1940's has revolutionized almost every facet of electronics. The benefits of this growth are apparent everywhere, from the clock-radios in homes to the powerful data processing equipments which are now an integral part of our schools and businesses. All phases of scientific research have already benefited from improvements in instrumentation through the use of transistors and integrated circuits. The instruments available today are more compact, more reliable and less expensive than their predecessors. Some of the developments in solid state electronics which show promise for application to a portable photomenter are the light emitting diode, the photo-diode, the photo-transistor and the integrated circuit operational amplifier.

Light Emitting Diode

The light emitting diode (LED) possesses a special p-n junction which emits light under forward bias. Electrons in the donor level below the conduction band of the junction move to the acceptor level above the valence band and lose energy in the process. This energy is emitted as radiant energy, either in the infrared or the visible region. The spectral position of the emitted light is related to the band energy gap in the semiconductor. The bandwidth is related to differences in energy of the donor level and the conduction band as well as the difference between the acceptor level and the valence band. LEDs are commonly made of GaAs doped with one or more of a variety of impurities. The LEDs first built emitted in the 900nm region. The most commonly available LEDs emit red light at approximately 670nm with a half-width of 25 nm (3). Only red, green and yellow LEDs are commercially available at present in the visible range, but orange, blue and violet emissions have been achieved in laboratories (4,5,6). Research is also being conducted with variable wavelength emission (7). With the current volume of research being conducted in the area, there is little doubt that LEDs covering the entire visible spectrum will be developed. The low power requirements of the LED (typically 15 milliwatts) coupled with the rather respectable luminous intensity of 100-500 lumens make its use in a photometer quite feasible. The effective bandwidth of the emitted light (Figure 2) is such that a monochromator is not required. Without the loss in radiant energy in a monochromator, all emitted energy is available to



Filter Transmittance Curves



LED Emission Curve

Figure 2. Comparison of the LED Emission Spectrum with the Transmittance Curves of Filters.

interact with the sample. The light source, power supply and monochromator of the typical photometer can thus be replaced by a simple flashlight battery, a current limiting resistor and the LED.

Photodiode

Photodiodes have been employed as photodetectors by Flaschka and co-workers in a variety of instruments (8,9). The photodiode operates on the principle that light impinging on a p-n junction affects the current carrier population in a semiconductor. When a photodiode is biased in the reverse mode, reverse current is quite small in the absence of light. In the presence of light, however, there is a significant increase in reverse current. Neglecting the "non-light" reverse current, the photocuttent is proportional to the light intensity (10). This photocurrent can be amplified and fed to a readout device. Although the photodiode has had imminent success as a photodetector, a device exists which exhibits even more sensitivity.

Phototransistor

The phototransistor (PT) is an extension of the photodiode concept. A photodiode form the base-collector junction of the transistor. The PT provides current gain for the photodiode junction and thus increases sensitivity. The relationship of the PT to the photodiode is analogous to that of the photomultiplier tube to the phototube (11). The use of the phototransistor in the place of the photomultiplier allows one considerable savings in weight, bulk and power requirements. Due to the ability of the PT to detect low light levels, low intensity light can be used and heating of the sample is minimized. The output of the PT is quite compatible with integrated circuit amplifiers, permitting the construction of a neat and rugged detection, amplification and metering system.

Integrated Circuit Operational Amplifiers

The advent of micro-miniaturization of electronic components has resulted in the availability of entire amplifier circuits contained in a can no bigger than a pencil eraser. One type, the operational amplifier, permits custom tailoring of the amplifier by varying external components so as to produce the desired gain. Power requirements are low and high stability of the output is observed.

The Solid State Photometer

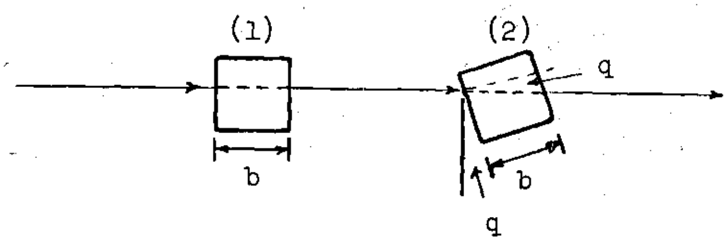
The small size, light weight and low power requirements of these solid state devices make it possible to construct a photometer using modular concepts, similar to systems used in television and audio equipment. Such a photometer consists of two main modules: (a) a cell module, consisting of the cell, the LED light source and the PT photodetector, housed in a light-tight box, and (b) a control module, consisting of the necessary power supplies, amplifiers and metering devices. Each module will be discussed in detail in subsequent chapters. A completely portable, modular solid state photometer has been constructed and has shown satisfactory performance.

CHAPTER II

CELL MODULE

General

One problem in practical photometry is the reproducible orientation of the cell in the light beam. As illustrated in Figure 3, if the sample cell does not have the same orientation for all readings, the physical path length through the cell will change, resulting in a change of the percent transmittance. One approach to remedy this problem is to use precision made cells and a cell holder machined to very close tolerances. This can be a pains-taking and expensive proposition. A novel approach is suggested by the small size and light weight of the LED and the PT. These may be affixed directly to the walls of the cell, forming a unit in which the physical path length cannot change. All that is required to complete the cell module are a supporting base and plugs to provide for electrical connections. Using this modular concept, when one desires to change the wavelength of the light source or the path length of the cell, one merely replaces the module with one possessing the desired parameters. A typical module is shown in Figure 4. At first reading, it would appear that use of this modular concept could be an expensive proposition. It should be realized that in a standard design, precision made cells with carefully ground and polished plane parallel walls are used in conjunction with precision machined cell holders. These items are quite



For Cell (1) path length = b

For Cell (2) path length = b/cos q

Figure 3. Effect of Misalignment of Photometric Cells.

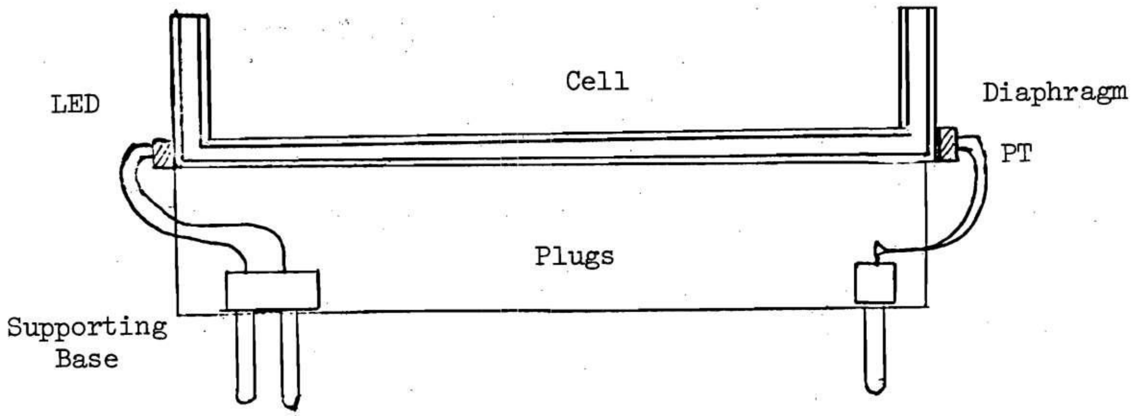


Figure 4. The Cell Module.

expensive, On the other hand, the cost of LEDs and PTs and the other components of the module is so modest that several cell modules can be fabricated for less than the cost of a single standard cell. When one considers the much higher cost of precision made long path cells, the economic advantage of the cell module concept becomes even more apparent.

Long Path Cells

It is perfectly feasible to affix the LED and the PT to a standard 1 cm cell and produce a workable module. However, the high sensitivity of the PT makes it possible to employ long path cells similar to those described by Flaschka and Barnes (12) and thereby permit the determination of lower concentration levels than is possible with a 1 cm cell. In order to study the feasibility of the modular approach over a varying range of concentrations, cell modules with 10, 20 and 30 cm path lengths were fabricated.

Construction of Cells

The original cells for the module were constructed in the following manner. A body tube of the appropriate length was cut from 4 mm inner diameter glass tubing. T-joints were made close to the ends of the body tube to provide entry and exit tubes for the solution. Clear glass windows were cemented to the ends of the body tube with both ordinary clear cement (DuPont Duco) or common epoxy cement. Cells made in this manner proved completely satisfactory for aqueous solutions. However, when operating with organic solvents, it was found that the cement securing the end windows was attacked and the windows fell off. Subsequent investigations revealed two approaches which successfully remedied the problem.

Solvent-Resistant Cement

Advances in the science of adhesives has produced a variety of "super-glues". One such adhesive, which is resistant to organic solvent attack is CIBA 6005 (13). To construct a cell, prepare a body tube with entry and exit tubes. Cut the ends of the body tube and grind them flat as close as possible to the joints. Prepare the CIBA 6005 by mixing 100 parts by weight of resin with 28 parts of hardener. An amount just sufficient to thinly cover the ground surface is applied to one end of the body tube. A thin piece of clear glass (microscope slide cover glass) is pressed onto the end, taking care that no cement is squeezed onto the inner surface of the window. If the window is not found to be clear, remove the glass and repeat the procedure with less cement. Keep the cell upright and allow to cure for 24 hours at room temperature. After curing, repeat the procedure to affix a window to the opposite end of the cell. When both windows are cured, trim the excess glass from around the ends.

All Glass Cell

A second remedy for solvent attack is the fabrication of a cell composed of glass only. This process is more difficult than the solvent resistant cement approach, but once constructed, the cell is practically impervious to attack by solvents. The body tube is prepared in the same manner as the previous procedure. One end is heated and sealed with a small bead of molten glass. By puffing gently, the bead is flattened on the inside. The procedure is repeated at the opposite end and the cell is annealed to relieve stresses in the glass. The ends are then ground flat and are polished to smooth and optically clear surfaces.

Mounting the LED and the PT

The small size and the light weight of the LED and the PT permit their attachment directly to the end windows of the cell. The LED employed is a MV-1 manufactured by Monsanto. The PT is a Fairchild FPF-130. The specifications for these devices are included in the Appendix. The LED and the PT are cemented in place with fast setting epoxy (Devcon #R-205) or a clear general purpose cement (DuPont "DUCO"). A diaphragm is placed between the PT and the end window to insure that no light which is transmitted through the walls of the body tube reaches the PT. The application of the cement extends for 1 cm along the sides of the body tube to increase mechanical strength. To improve the adhesion of the cement to the glass, the sides of the body tube were roughened with emery paper.

Supporting Base

The sample cell with the LED and the PT affixed is mounted on a support fabricated from 3 mm plexiglas. Two double pin plugs (Archer #274-342) are affixed to the support to provide for electrical connection of the LED and the PT to the wiring of the lightproof housing. The orientation of the plugs is such that improper electrical connection of the module is avoided. The distance between the plugs is the same regardless of the length of the module. This permits the use of a single set of input jacks in the housing to accept any of the modules.

Lightproof Housing

There are elaborate means by which the effects of ambient light on the photodetector may be excluded, some of which will be discussed in a later chapter. However, a simple, yet effective method is to enclose the cell module in a lightproof housing (Figure 5). The inner dimensions of the housing are selected to accomodate the longest cell module used. Two jacks in the base of the housing accept the corresponding plugs on the cell module. The distance between the jacks is determined by the shortest module used. The jacks are wired to external jacks for connection to the control module. A microswitch in the PT circuit opens when the door to the housing is opened, preventing the strong ambient light from overloading the PT and the amplifier. To prevent the entry of reflected light, the door is fitted with weatherstripping and the entire inner surface of the housing is painted flat black.

Filling and Emptying of Sample Cells

For convenience in filling and emptying sample cells, a thistle is fitted to the entry tube of the module and a tygon tube is fitted to the exit tube. This tube is passed through the wall of the housing and is connected to a receiving vessel. Emptying of the cell is

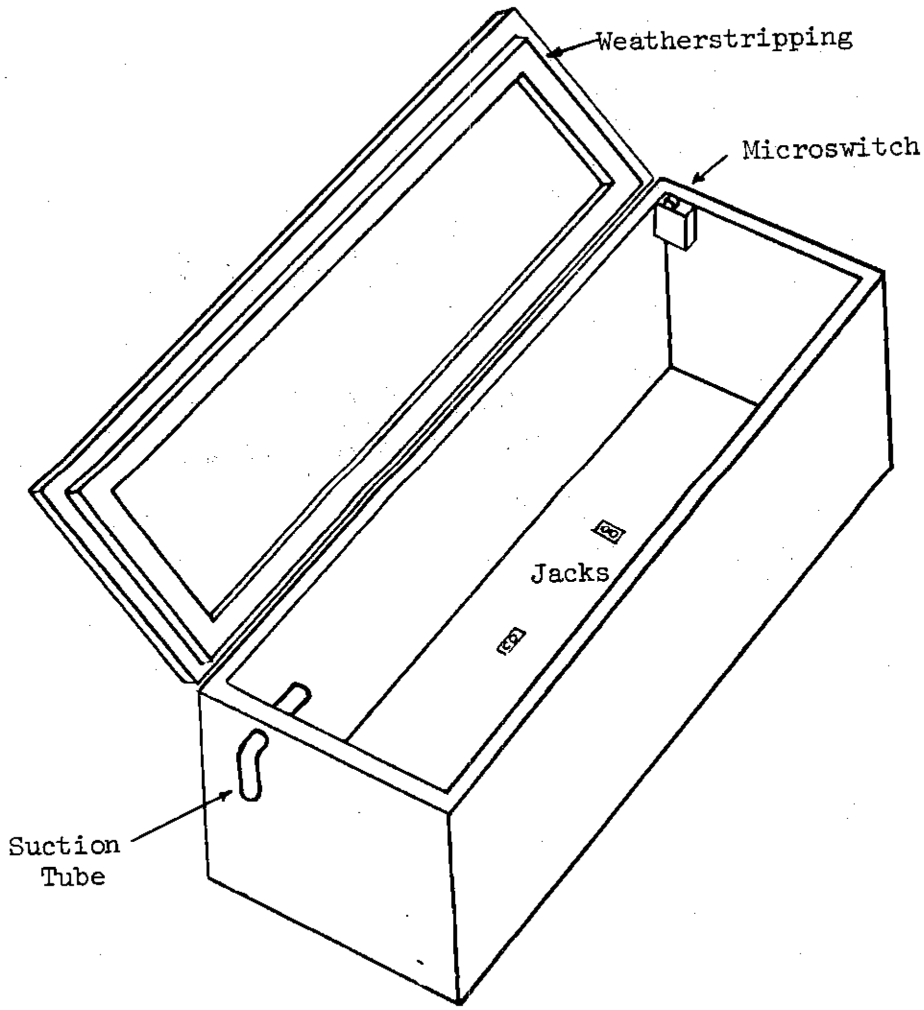


Figure 5. Cell Module Housing.

accomplished by suction. Separate receiving vessels may be used to retain the sample for further operations or a single vessel may be used for discardable samples.

CHAPTER III

CONTROL MODULE

The control module for the solid state photometer contains the power supply and control circuit for the LED, the power supply and circuit for the PT, the amplifier to boost the photodetector output signal and the meter.

LED Power Supply and Circuit

As already mentioned one of the advantages of using a LED as the light source is its very low power requirement. The power source consists merely of two 1.5 volt flashlight batteries connected in series to provide 3.0 volts. This power supply, a fixed resistor, a variable resistor and two jacks are connected as shown in Figure 6. The fixed resistor limits the current to a safe value, preventing burnout of the LED. The variable resistor permits the adjustment of the current and thus the intensity of the emitted light. This feature is used to set 100 percent T. Correct polarity of the power supply must be observed as the LED will emit light only under forward bias. The jacks are mounted on the control module housing and are color coded to facilitate correct connection to the corresponding jacks located on the cell module housing.

PT Power Supply and Circuit

The power supply for the PT circuit is identical to that of

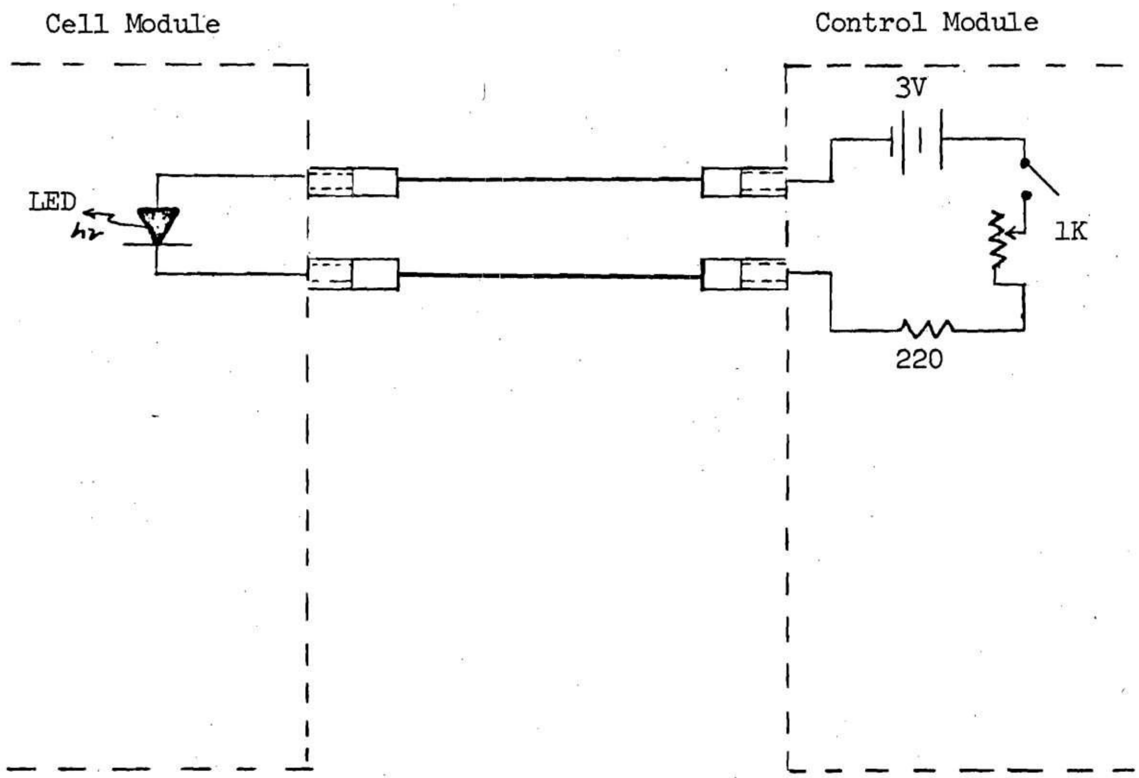


Figure 6. LED Circuit.

the LED circuit. It is possible to use the same power supply for both circuits, but the use of separate power supplies provides electrical isolation of the circuits and prevents any interaction between them except through the cell module. The batteries, a load resistor and two jacks, are connected as shown in Figure 7. As in the LED circuit, the jacks are mounted on the control module housing and are color coded to the corresponding jacks on the cell module housing. Light impinging on the PT causes current flow. The voltage drop across the load resistor is proportional to the intensity of the light and may be measured with a sensitive galvanometer. When the signal is to be amplified prior to readout, the load resistor is deleted from the circuit.

Detector Signal Amplifier

The use of a laboratory type galvanometer is obviously not in consonance with the goal of portability. It is therefore necessary to amplify the detector current to drive a less sensitive, but more portable and rugged meter. The maximum output current of the PT circuit is approximately 0.4 microamperes. In order to drive a meter requiring 250 microamperes for full scale deflection, a gain of 625 is required. If solid state devices were not so readily available, it would be difficult to achieve such gain while retaining reasonable stability and portability. One can design and build an amplifier from components, but a much simpler alternative is the use of an operational amplifier. Its small size, ruggedness and low power requirements make it appear to be ideal for this application. By incorporating a feedback

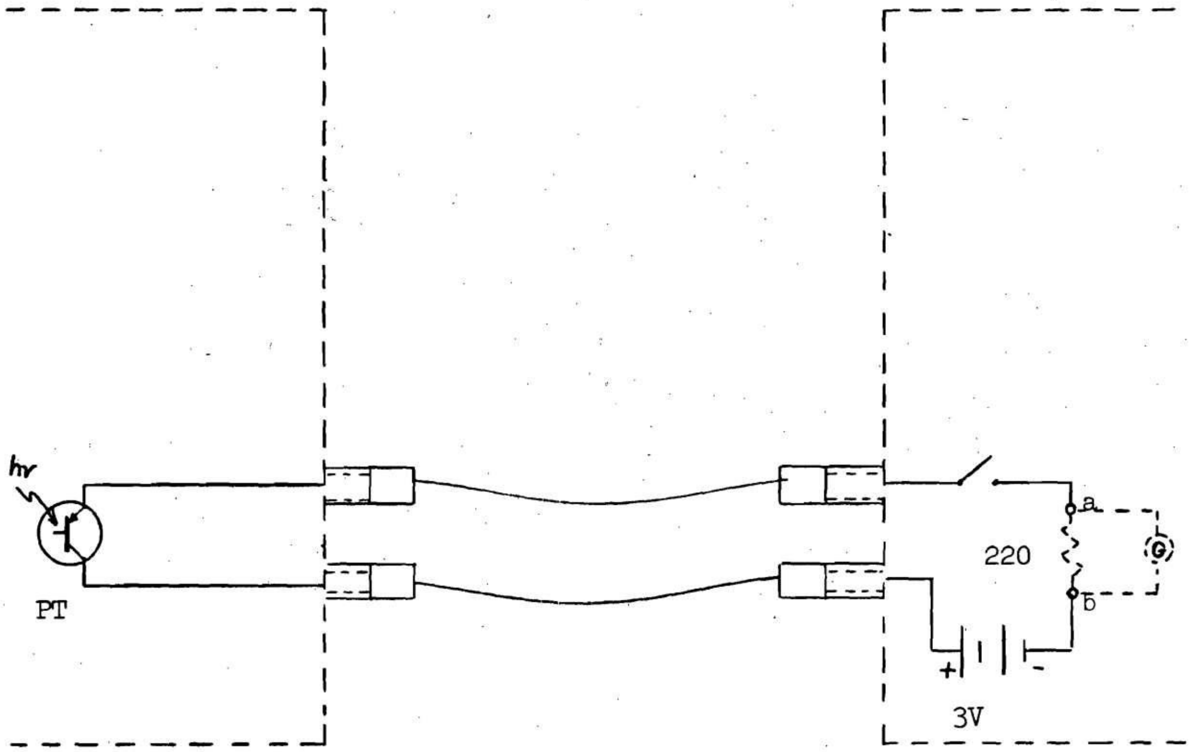


Figure 7. PT Circuit.

resistor of appropriate value, the desired gain can be obtained. An operational amplifier which was found to meet the requirements for the present application is the Fairchild 740C. Specifications for this device are contained in the Appendix. The 740C provides high gain, stability and linearity as well as ruggedness, an important consideration when seeking portability. The complete amplifier circuit is shown in Figure 8. The 1 megohm feedback resistor was selected to provide the desired gain of 625. The 1.47 K-ohm resistor adjusts the meter current to the range that is correct for the meter employed. The remaining portion of the circuit is the zero adjust feature. This is a simple voltage divider network which allows one to feed sufficient current to the input of the operational amplifier to cancel the dark current of the PT circuit. The variable resistor is simply adjusted until the meter reads 0 percent T. The power supply for the amplifier consists of four 7.0 volt mercury batteries (Eveready #E165) connected in series. The power supply is center tapped for ground and end tapped for + and - 14 volts.

Meter

There are numerous types of readout devices such as digital meters, strip chart recorders, etc., which might be adapted to this photometer. However, in keeping with the objectives of ruggedness, portability and low cost, a simple moving coil type panel meter was selected. The meter used is identical to that used in the Bausch and Lomb Spectronic 20 photometer (Assembly Products, Inc., Model 451). The face of the meter is provided with a linear scale for

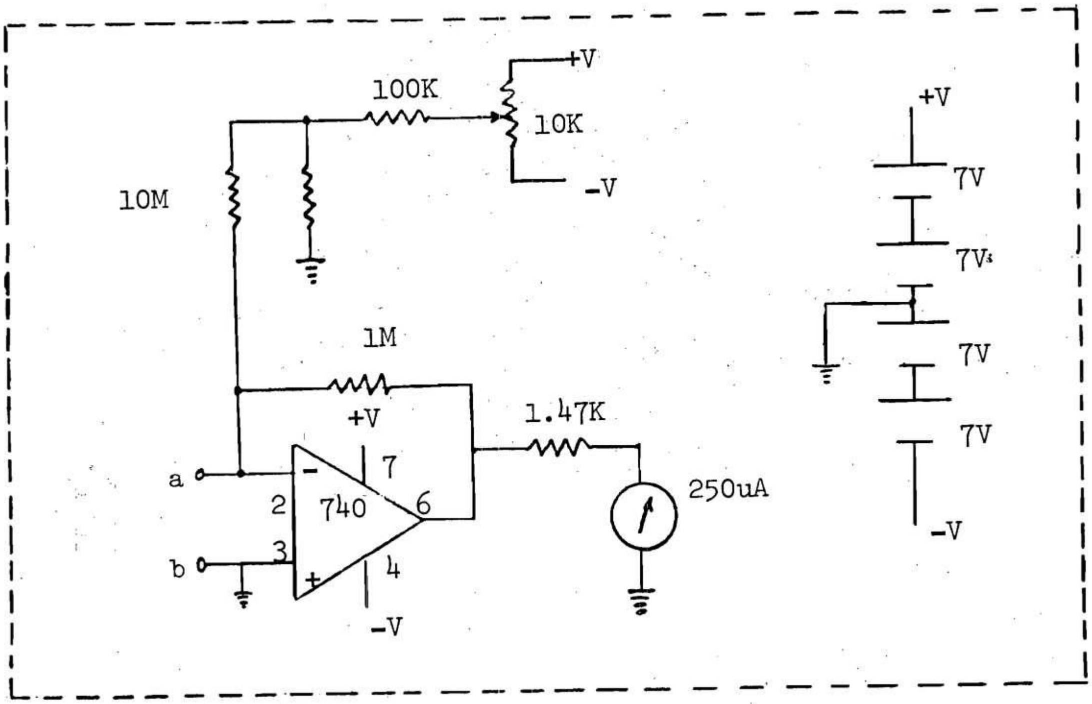


Figure 8. Amplifier Circuit.

percent transmittance and a corresponding logarithmic scale for absorbance. The ultimate in weight and cost savings could be realized by replacing the metering and amplification systems by a null meter and a precision helipot in a bridge circuit. Fewer and less expensive components could be used.

Housing

All components are mounted in an aluminum box (8" x 6" x 3½", BUD #CU-3009-A)(Figure 9). The meter is mounted at a 45° angle to the top of the housing. This position improves the readability of the meter. Three switches are mounted on the front of the housing. One connects the operational amplifier to its power supply and is marked "Master Power". The other two control the LED and the PT, respectively. Three knobs are mounted on the top of the housing. The leftmost knob controls the zero setting. The others provide coarse and fine adjustment of 100 percent T. The four colored coded jacks on the rear of the housing have been previously discussed.

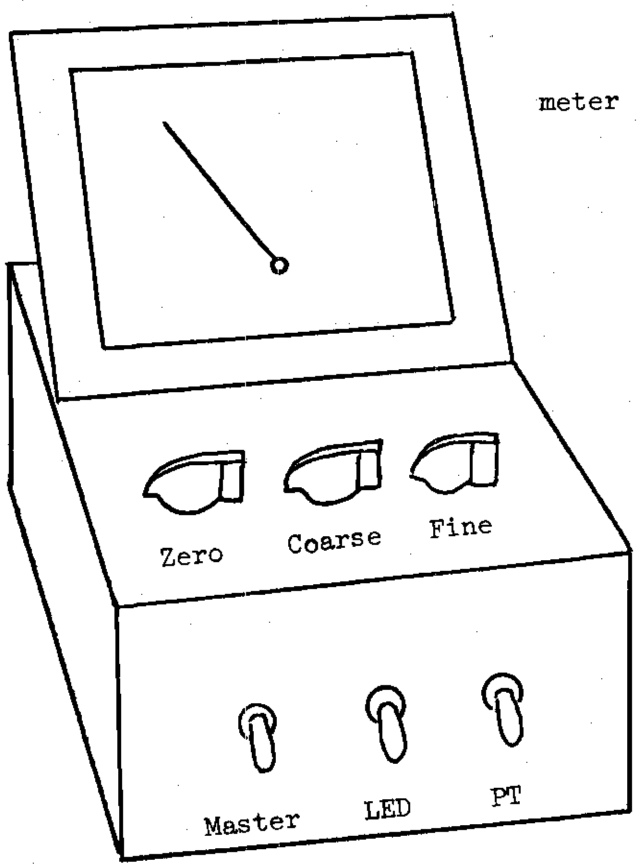


Figure 9. Control Module

CHAPTER IV

OPERATING INSTRUCTIONS

The procedure outlined below is based upon the use of a calibration curve technique.

Equipment Set-up

(1) Assure that all switches on the control module are in the "OFF" position.

(2) Connect the LED and the PT jacks on the control module to the corresponding jacks on the cell module housing. Use the color coding of the jacks to assure correct polarity.

(3) Connect the receiving vessel to the outlet tube with tygon tubing.

(4) Select a module with the appropriate path length and plug it into the cell module housing. Connect the outlet tube to the cell module.

Operation

(1) Fill the cell with the blank (approx. 4-5 ml). By puffing gently into the suction tube of the receiving vessel, air bubbles may be eliminated from the cell. Close the door of the housing.

(2) Place the master power switch and the PT switch in the "ON" position. Adjust the zero knob to achieve "0 % T" on the meter.

(3) Place the LED switch in the "ON" position. Set 100 % T on

the meter by adjusting the coarse and fine 100 % T knobs.

(4) Recheck the zero setting by placing the LED switch in the "OFF" position. Return the LED switch to the "ON" position for all subsequent operations.

(5) Open the housing door. Empty the cell by suction and place 1-2 ml of the first standard in the cell. Apply gentle pressure and suction alternately to move the liquid back and forth, thereby rinsing the cell, then empty the cell.

(6) Fill the cell with 4-5 ml of the standard and assure that no air bubbles are present in the body tube. Close the door and record the meter reading.

(7) Repeat steps 5 and 6 with each of the standards and then with the unknown solution.

(8) Repeat steps 5 and 6 with the blank. Compare the meter reading with that observed in step 3 to check for drift.

(9) Place all switches on the control module in the "OFF" position and rinse the cell with an appropriate solvent.

(10) Treat the recorded data in the usual manner.

Note

When wearing apparel that may generate static electricity, the operator may observe momentary fluctuations in the meter reading when he moves. This is due to the amplification of the static electricity and has no effect on the final reading. This effect may be avoided by remaining motionless while making readings.

CHAPTER V

PERFORMANCE TESTING AND CONCLUSIONS

In order to evaluate the practicality of the solid state photometer, it was tested in the following areas: (a) stability, (b) linearity of response, (c) reproducibility of readings, (d) light tightness of the cell module housing and (e) portability.

Stability

For the present purposes, we may define short term stability as the constancy of readings during time frames less than a minute and long term stability as the constancy of readings during longer periods. The stability of the individual electronic components, that is, the phototransistor, the LED and the amplifier, each contribute to the overall stability of the instrument.

The stability of the phototransistor must be evaluated in regard to the dark current and the light current. Dark current occurs because the phototransistor does not provide infinite resistance at zero illumination, thus a small amount of current flows. The zero adjust portion of the amplifier circuit is designed to compensate for this dark current. To evaluate the dark current stability of the PT, the circuit shown in Figure 7 was used in connection with a Leeds-Northrup No. 2430 DC galvanometer. Short term fluctuations of the dark current were not detectable. Long term drift was less than $\pm$ 0.5

scale divisions over a period of four hours.

Light current stability was evaluated by exposing the PT to a stable light source at several levels of luminous intensity for a period of one hour. The stable light source was provided by connecting an incandescent lamp to six lead storage batteries connected in parallel. The batteries were freshly charged and the lamp was permitted to burn for 30 minutes before beginning the test to assure that a stable condition was reached. An adjustable comb was used to vary the intensity of the light reaching the PT. A strip chart recorder was connected to the output of the PT to produce response tracings. The recorder was run at zero input signal to check for drift and fluctuations in the recorder. Test runs were made with the lamp output adjusted to produce recorder pen deflections of 20, 40, 60 and 80 scale divisions. After each run, the chart paper was rerolled to permit the tracings to be made side by side. The tracings reveal no detectable short term fluctuations or long term drift (Figure 10).

The stability of the LED was evaluated by replacing incandescent light source used in the preceding test by the LED circuit described by Figure 6. Since the PT circuit was found to be reasonably stable, it was used to evaluate the stability of the LED circuit. A strip chart recorder was used in the same manner as the preceding test. The LED output was adjusted to produce recorder pen deflections of 25, 45, 65, and 85 scale divisions. Short term fluctuations were not detectable. Long term drift was less then $\pm$ 0.5 scale divisions. (Figure 11).

The stability of the amplifier was checked by preparing the

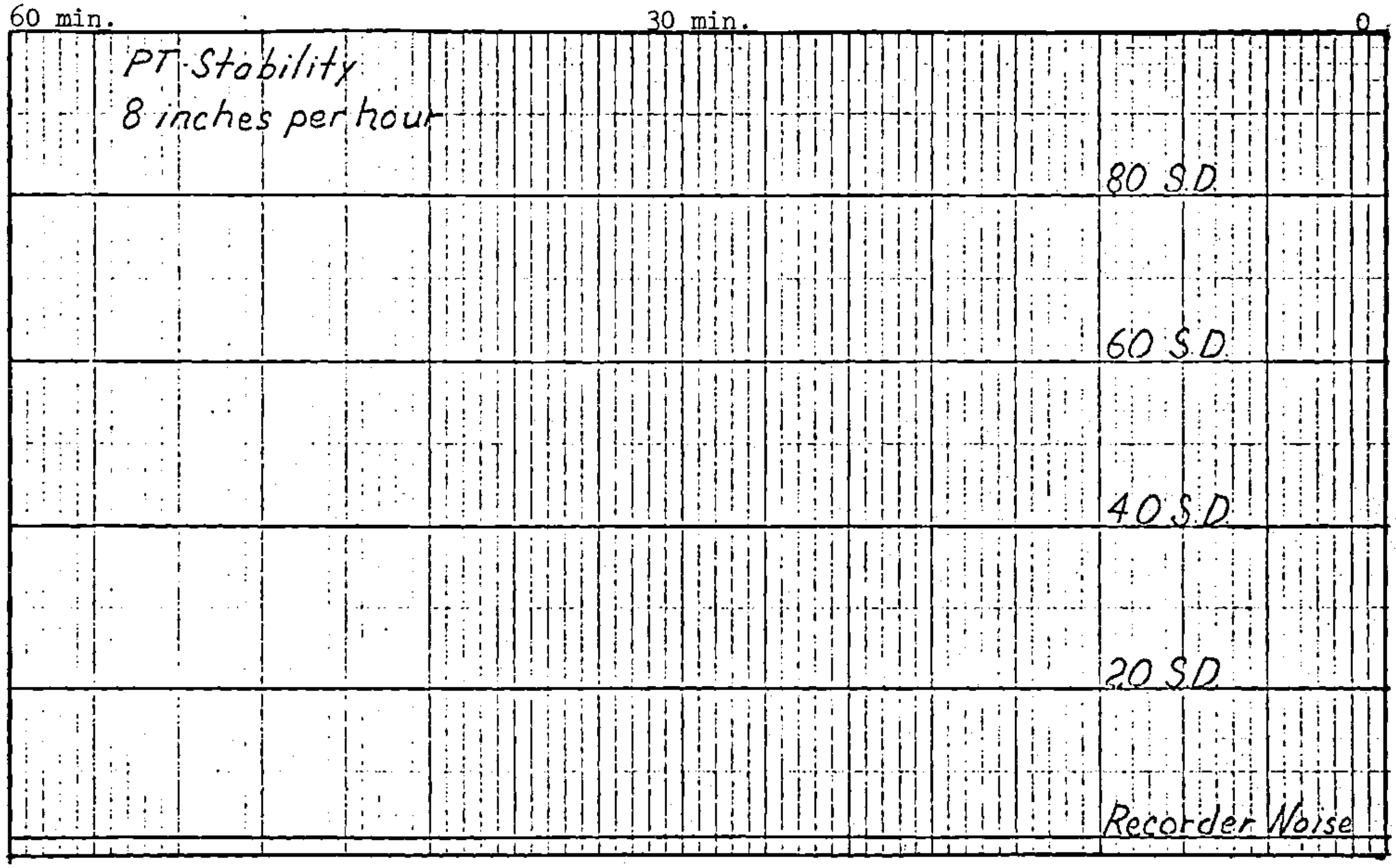


Figure 10. PT Stability

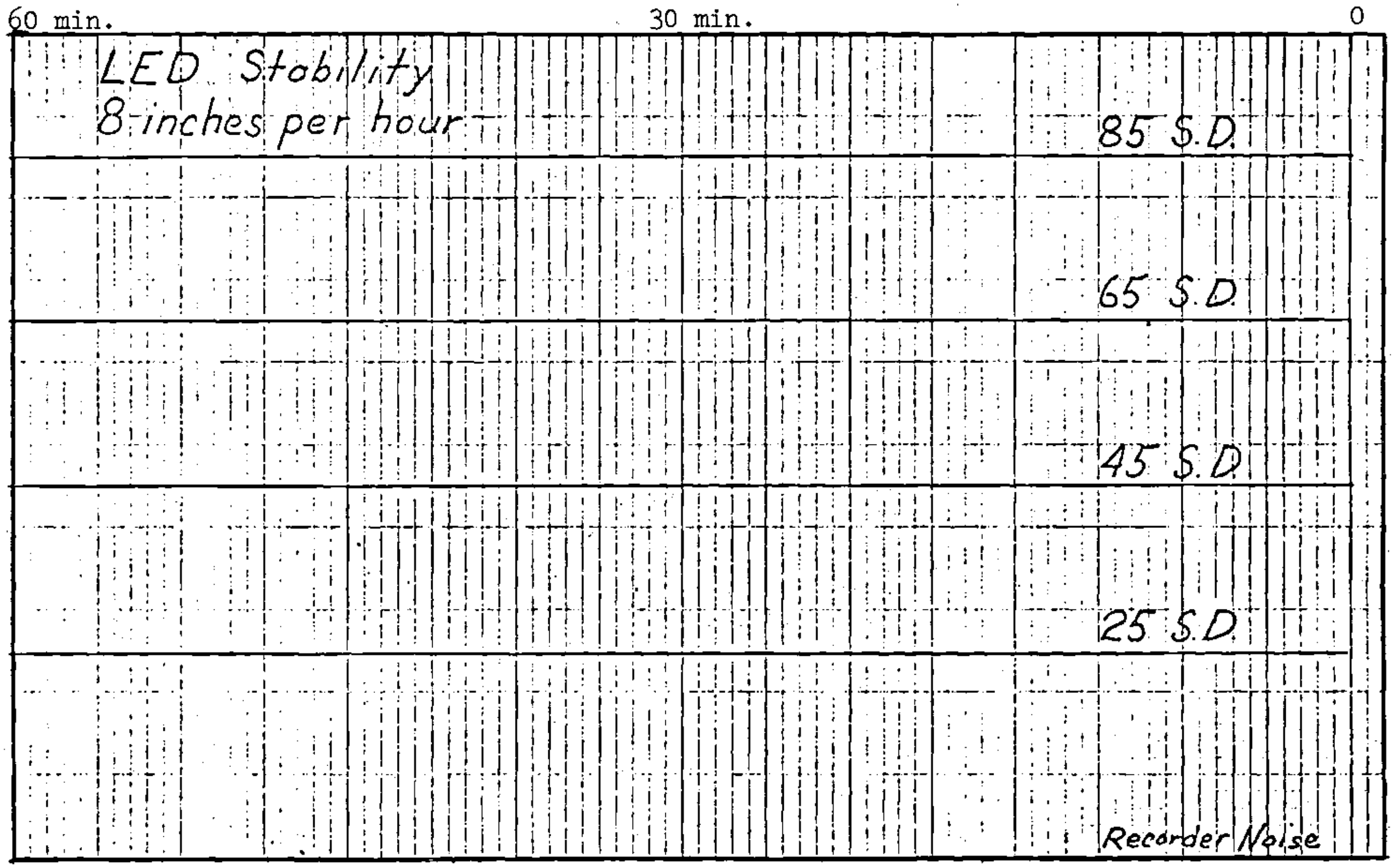


Figure 11. LED Stability

photometer for operation as described in the operating instructions. A strip chart recorder was then connected in parallel with the meter on the control module. The instrument was operated at various levels of percent transmittance and the amplifier output was recorded. Examination of the traces revealed less than $\pm$ -0.5 scale division fluctuations over a four hour period. Some momentary noise was observed, but this was found to be due to the amplification of bursts of static electricity (Figure 12).

The minor deviations noted in the above tests were considered to be well below the levels that would seriously hamper the use of the instrument in field operations.

Linearity of Response

Linearity of response is dependent on three factors: (a) the monochromacy of the light, (b) the relationship of the output of the PT to the intensity of the luminous flux and (c) the linearity of the amplifier. Because of the lack of adequate instrumentation to verify the spectral characteristics of the LED, the data published by the manufacturer were taken to be applicable.

The linearity of the PT was evaluated in the following manner. A stock solution 0.05 F in Cu^{+2} was prepared by dissolving 12.1 grams of cupric nitrate (Baker, Analyzed Reagent Grade) to one liter in doubly deionized water slightly acidified with three drops of concentrated nitric acid. One, two, three, four and five ml aliquots of this stock solution were diluted to 100 ml in volumetric flasks and were used as standards. The PT circuit was connected as shown in Figure 7

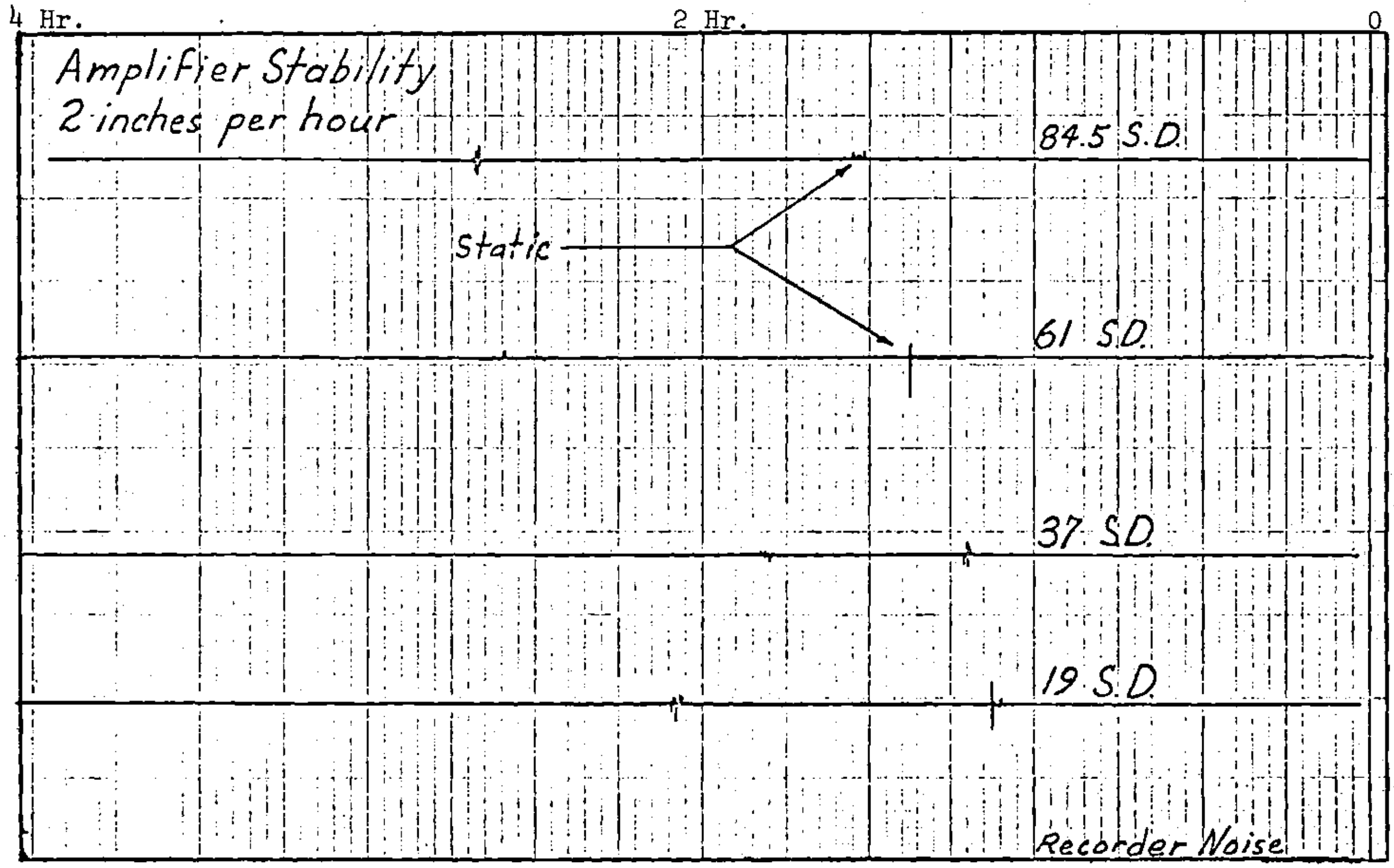


Figure 12. Amplifier Stability

with the galvanometer in the circuit. Deionized water was placed in the cell and the LED intensity was adjusted to produce a scale reading of 100 divisions. Readings were then taken for each of the standards, and absorbance was plotted versus ml of stock solution. This procedure was repeated for each module size. As illustrated in Figure 13, each of the plots yields a straight line passing through the origin, thus indicating adequate monochromacy and linear response of the PT.

The amplifier was checked for linearity by connecting the photometer as described in the operating instructions and repeating the above procedure. Once again, straight line plots passing through the origin were obtained (Figure 14), indicating linear amplifier response.

Reproducibility of Readings

Due to the high gain of the amplifier, it was believed that small variations in the contact resistance of the plugs, connectors, jacks and switches might result in major variations in meter readings. To evaluate this, the strip chart recorder was connected across the meter inputs and the LED was adjusted to yield mid-scale deflection of the recorder pen. Each of the switches was operated several times. The connecting cables were disconnected and reconnected a number of times. Carefully avoiding any turning of the knobs on the control module, the entire photometer was disassembled into its components and reassembled. After each of the above actions, the recorder pen immediately returned to its initial position (Figure 15).

Reproducibility of a given value was determined by repeated measurement of a single standard solution. A transmittance value was

Table 1. Comparison of Absorbances Read for Varying Path Length Cells with varying Cu^{+2} Concentration (Simple PT Circuit with Galvanometer Readout).

ml stock	Absorbance Units 10 cm	20 cm	30 cm
0	0	0	0
1	0.021	0.041	0.065
2	0.044	0.089	0.131
3	0.068	0.135	0.204
4	0.089	0.179	0.268
5	0.109	0.217	0.328

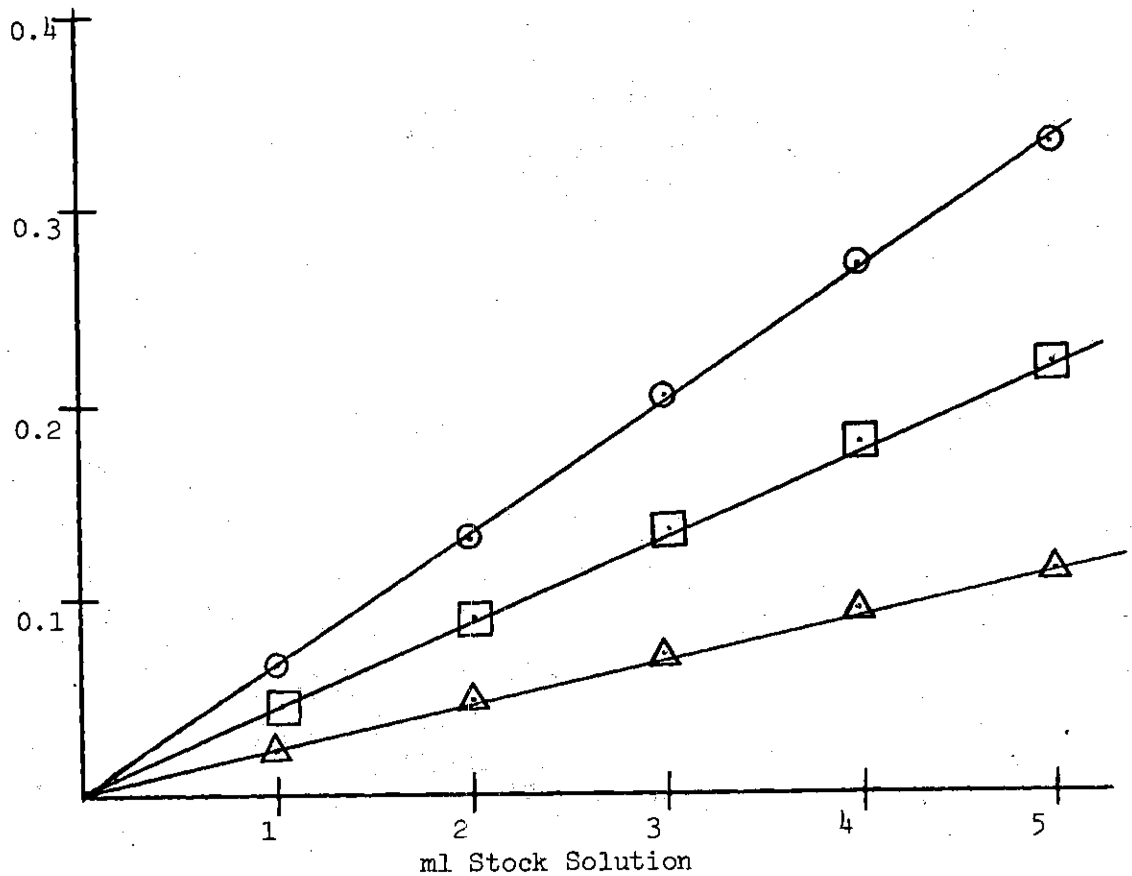


Figure 13. Absorbance vs. ml Stock with Galvanometer Readout

Table 2. Comparison of Absorbances Read for Varying Path Length Cells with Varying Cu^{+2} Concentration (Amplified Signal with Meter Readout).

ml stock	Absorbance Units		
	10 cm	20 cm	30 cm
0	0	0	0
1	0.019	0.039	0.057
2	0.041	0.084	0.123
3	0.060	0.124	0.179
4	0.078	0.157	0.235

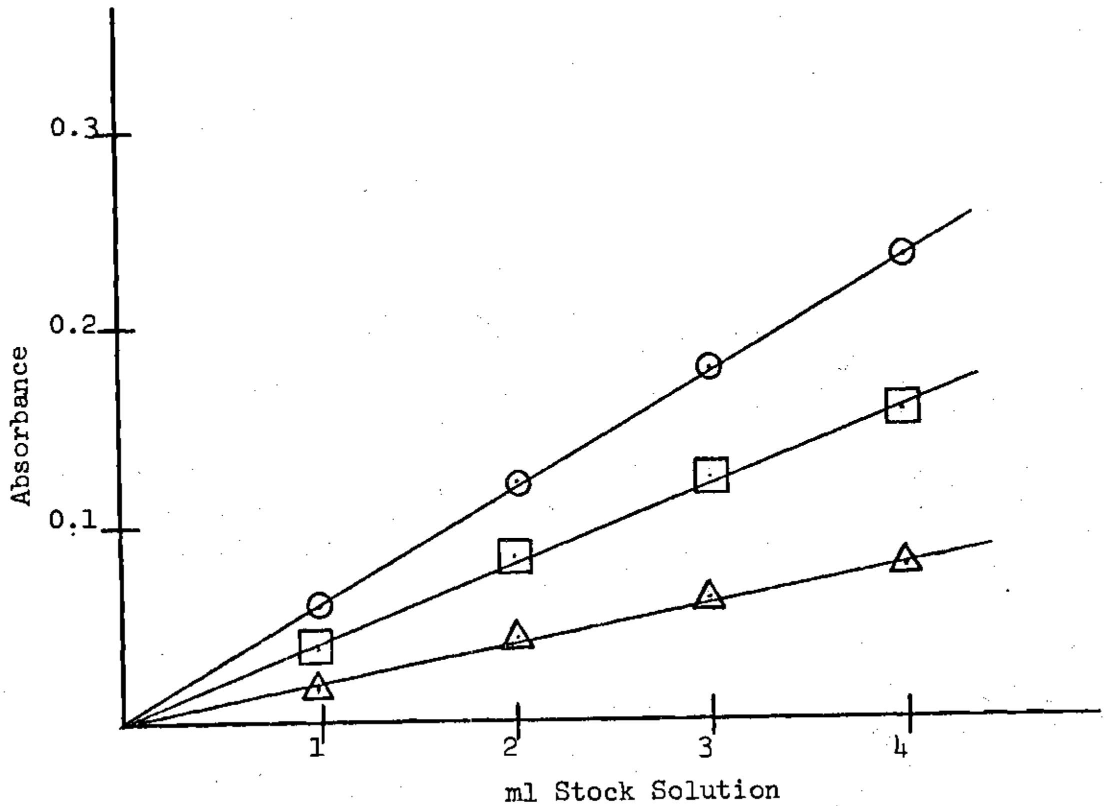


Figure 14. Absorbance vs. ml Stock with Control Module Readout

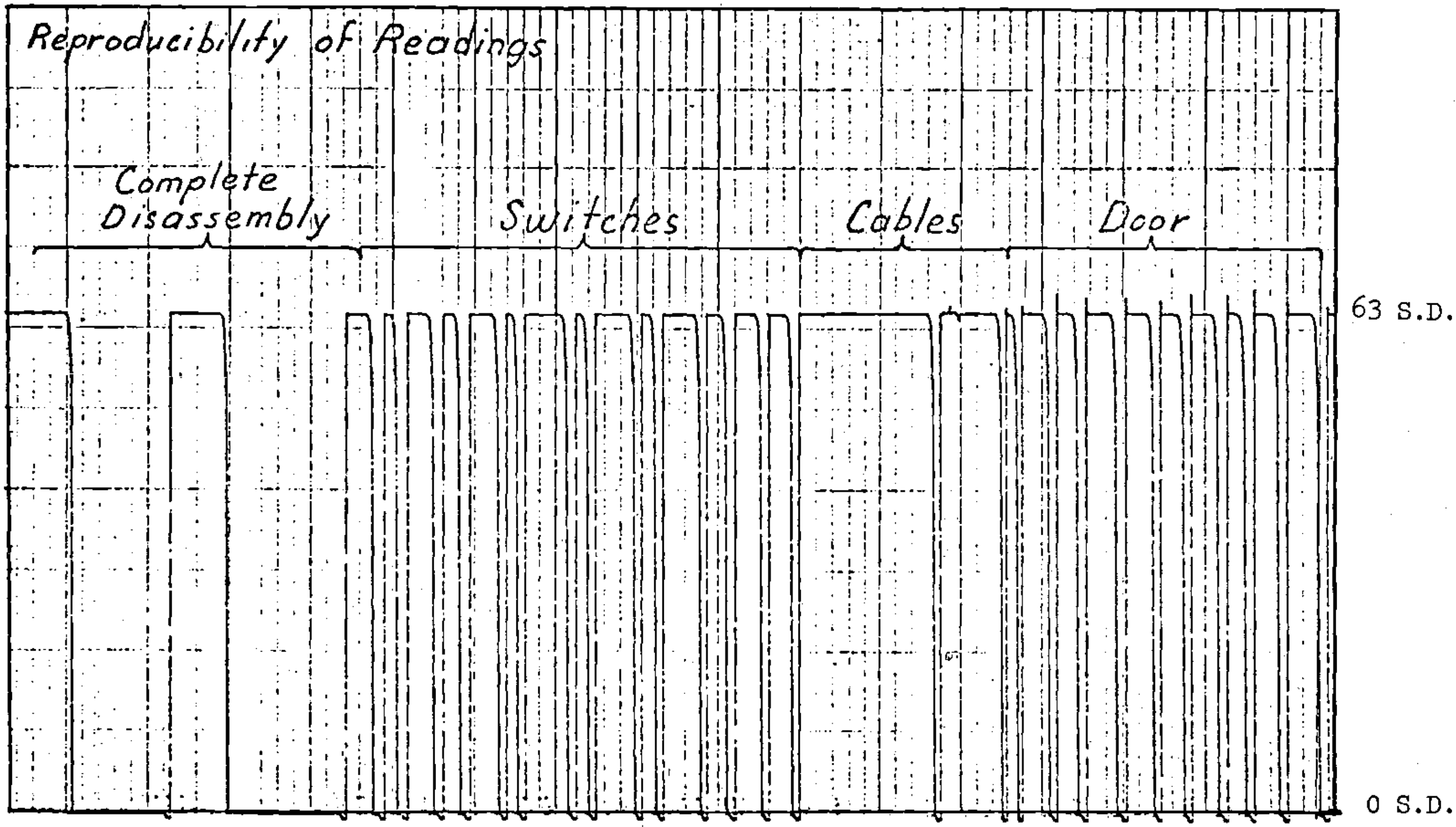


Figure 15. Reproducibility of Readings

determined, the standard was replaced by another portion and the transmittance read again. This procedure was repeated 10 times. The results are shown in Table 3.

Lighttightness

The ability of the cell module housing to exclude ambient light was evaluated by passing a 100 watt light bulb around the door, six inches from the edges. Deviations in the meter readings did not exceed 1 1/2 scale divisions. The photometer was taken into direct sunlight and operated under different conditions of light and shade. No variations in the meter readings were noted.

Portability

The small sizes and light weights of the modules render the photometer easily portable. The cell module housing is 44 x 218 x 18 cm and weighs four pounds complete with the cell module installed. The control module measures 15 x 21 x 20 cm and weighs 3 1/2 pounds complete with batteries. One man can carry the entire assemblage with no difficulty.

Conclusions

The results of the above testing prove that the construction of a workable solid state photometer is quite feasible and practical. The device constructed has proven to be reliable and rugged. Numerous determinations have been made using the calibration curve method. Additionally, photometric titrations of copper with EGTA have been performed (Figure 16).

Table 3. Reproducibility of a Given Value

Sample No.	% T
1	65.50
2	65.25
3	65.75
4	65.75
5	65.50
6	65.75
7	65.25
8	66.00
9	65.50
10	65.25

Average = 65.55

Single Value

Std. Dev. = 0.2581

Variance = 0.0667

Ave. Dev. = 0.21

Rel. Std. Dev. = 0.3939 %

Rel. Ave. Dev. = 0.3204 %

Average

Std. Dev. = 0.0816

95 % Conf. Int. = $\pm$ 0.1845

99 % Conf. Int. = $\pm$ 0.2645

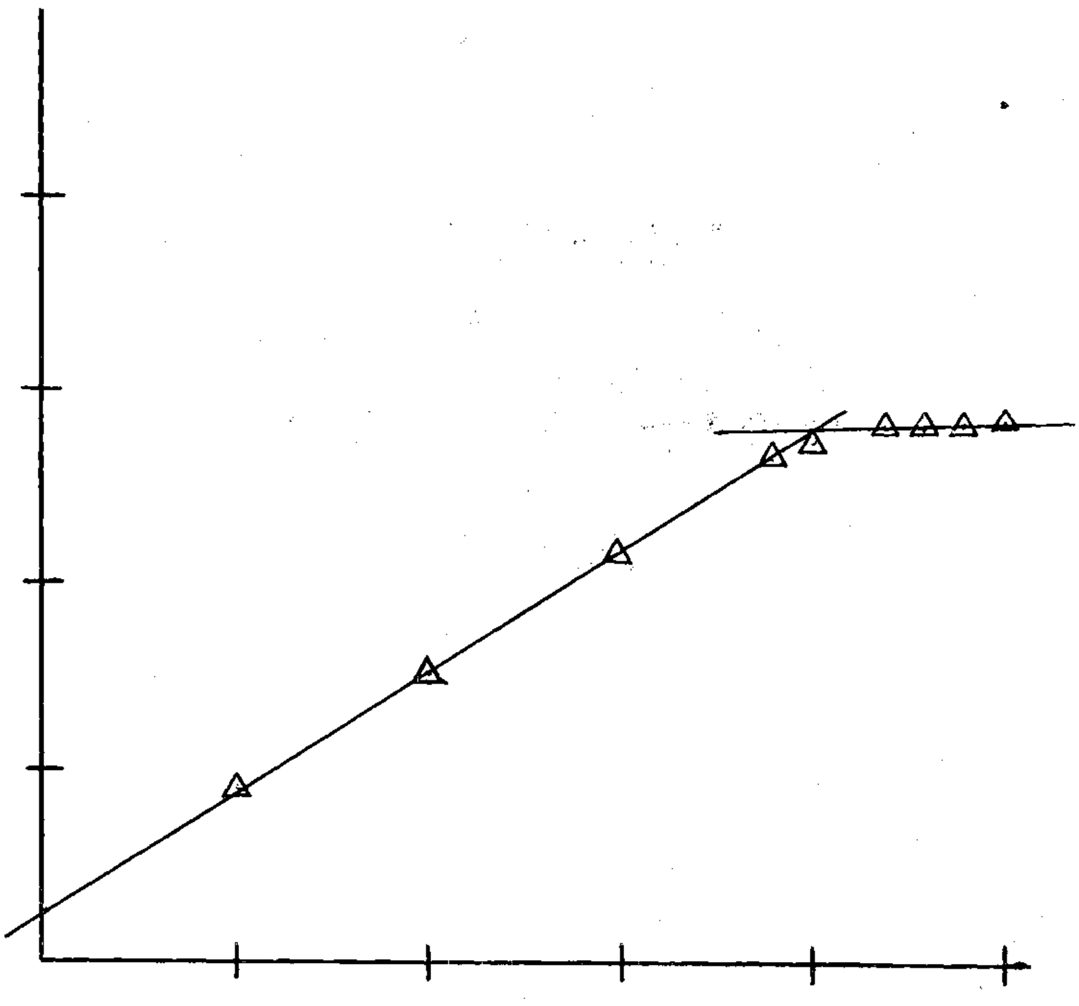


Figure 16. Photometric Titration of Copper with EGTA

The major disadvantage of the solid state photometer is the lack of complete coverage of the visible spectrum with the LEDs presently available, but, as previously noted, the development of LEDs providing such coverage is only a matter of time. Indeed, while this paper was being drafted, the introduction of an LED capable of emitting red or green light, depending on biasing conditions, was reported (14).

The advantages of the solid state photometer are its simplicity, portability, ruggedness and low power requirements. It can be constructed by anyone possessing a minimum of technical skills.

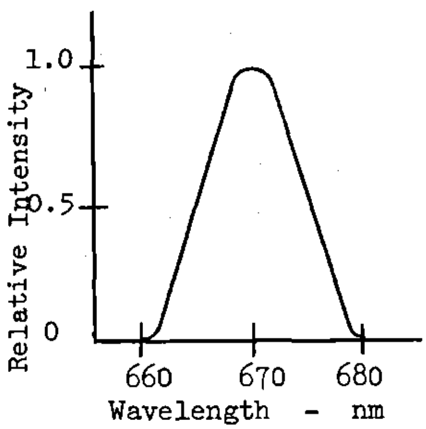
The solid state photometer has a variety of possible applications. It can be used as a simple long-path photometer for trace analysis under field conditions. With minor modifications, it can be used for on-line determinations in connection with an auto-analyzer or a liquid chromatograph. By constructing the cell module as a probe, turbidity measurements and dye spill monitoring in lakes and streams can be accomplished. Further applications are limited only by the imagination.

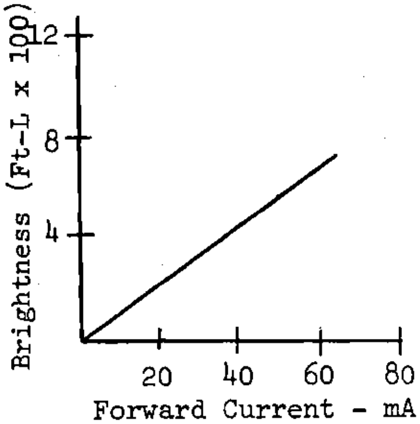
APPENDIX

A-1 Specifications - Light Emitting Diode (15)

TYPE - Monsanto MV-5320
PEAK WAVELENGTH - 670 nm
SPECTRAL HALFWIDTH - 25 nm
LUMINOUS INTENSITY - 700 Ft-L
MAXIMUM FORWARD CURRENT - 50 mA
MAXIMUM REVERSE VOLTAGE - 3.0 volts

Characteristic Curves





A-2 Specifications - Phototransistor (16)

TYPE - Fairchild FPF-130
COLLECTOR DARK CURRENT - 10 nA
PHOTOCURRENT (GaAS Source) - 4.5 mA
PHOTOCURRENT (Tungsten Source) - 9.0 ma

A-3 Specifications - Operational Amplifier (17)

TYPE - Fairchild μA740C
SUPPLY VOLTAGE - ± 14 volts
INTERNAL POWER DISSIPATION - 500 mW
INPUT RESISTANCE = 10^6 Megohms
MAXIMUM GAIN - 10^6
OUTPUT RESISTANCE - 75 ohms
INPUT VOLTAGE RANGE - ± 12 volts

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